Critical fluctuations and random-anisotropy glass transition in nematic elastomers

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We carry out a detailed deuterium NMR study of local nematic ordering in polydomain nematic elastomers. This system has a close analogy to the random-anisotropy spin glass. We find that, in spite of the quadrupolar nematic symmetry in 3-dimensions requiring a first-order transition, the order parameter in the quenched "nematic glass" emerges via a continuous phase transition. In addition, by a careful analysis of the NMR line shape, we deduce that the local director fluctuations grow in a critical manner around the transition point. This could be the experimental evidence for the Aizenman-Wehr theorem about the quenched impurities changing the order of discontinuous transition.

Introduction

The debate over the nature of the spin-glass phases in finite dimensions (and in experiment) is still vibrant in the modern literature [1, 2, 3]. The key question is about the nature of the symmetry that is broken by the spin-glass transition. The simplest idea is that the broken symmetry is the standard up-down, Ising symmetry. Even a random-anisotropy Heisenberg system apparently maps into the Ising spin glass [4]. Low energy excitations of arbitrarily large size confer critical properties to the system; in particular the non-linear susceptibility diverges in the whole spin-glass phase. However, because the up-down symmetry is sensitive to the external magnetic field, there cannot be a strict phase transition in non-zero field, only a dynamical crossover. In mean-field, or continuum models, on the other hand the broken symmetry is in fact the Parisi 'replica symmetry' [5], which encodes mathematically the presence of many possible ordered phases, unrelated to one another by simple transformations. The external field cannot select one out of a very large number of possible frozen configurations. Therefore in mean-field one expects, and indeed finds, a true phase transition even in non zero field – the celebrated de Almeida-Thouless (AT) line [6].

There has been relatively little study on how the quenched disorder influences the systems whose pure versions undergo a first-order phase transition. This question was first addressed by Imry and Wortis [7] who showed that inhomogeneities may cause local variations of the transition temperature inside the sample. Provided that the cost in interface energy is not great, bubbles of the 'wrong' phase are formed, eventually leading to a substantial rounding of the transition. A theorem due to Aizenman and Wehr [8] shows that in less than two dimensions in a system with quenched random impurities there can be no phase coexistence at the transition, and therefore no latent heat. Therefore these systems are expected to always exhibit a continuous transition. The influence of quenched impurities coupling to the local energy den-

sity has been extensively studied by Cardy [9]. It was found that, depending on the specific values of parameters of the pure system, such as the latent heat and the surface tension, the disorder-affected phase transition is fluctuation-driven and can either be first or second order. In both cases of spin-glass and quenched first-order systems the experimental measurement of equilibrium transition characteristics is very difficult and only few indirect results are available; most of the studies, such as neutron spin-echo experiments [10] only access dynamic quantities and correlation functions.

A physical system, in which the sources of quenched orientational disorder can be coarse-grained to be represented by a weak random field, is liquid crystalline elastomers [11]. Quenched disorder is intrinsically present in all elastomers as a direct result of their synthesis. In the simplest situation, the network crosslinking takes place in the isotropic phase, in which case the local anisotropy axis of each crosslinking group is randomly oriented [12]. Once the polymer network is formed, the configuration of the crosslinks remains quenched, and the underlying nematic [13] or smectic [14] phase transition takes place with their effect in the background. Other liquid crystalline systems with random disorder include the nematic in pores of silica gels [15], polymer-stabilized and polymer-dispersed liquid crystals, e.g. [16]. The source of the random disorder in such cases is the surface anchoring of nematic director on the walls of the random porous matrix on a length scale similar, or greater than the characteristic period of resulting director textures. In nematic elastomers the random disorder arises from defects in the polymer network structure and cross-links quenched during the synthesis, on a much smaller length scale, which allows for coarse-graining and the continuum mean-field description.

In this work we carry out the deuterium NMR experiments to measure the local nematic order parameter in the 'polydomain' nematic elastomer system, that is, the equilibrium symmetry broken state with the orientational texture fully analogous to the spin glass. Strictly, the nematic order parameter is a tensor with quadrupolar symmetry, arising from the averaging of axes $(\hat{\boldsymbol{u}})$

of rod-like molecular groups: $Q_{ij} = \langle \hat{u}_i \hat{u}_j - \frac{1}{3}\delta_{ij}\rangle = S(T)[n_i n_j - \frac{1}{3}\delta_{ij}]$ in three dimensions. In the system with quenched disorder one must distinguish between the time- and the ensemble averaging, since the principal axis $\boldsymbol{n}$ of this order parameter (called the nematic director) randomly varies in space. NMR is the only technique we know that can access the local value of the scalar order parameter $S(T)$ in spite of the powder averaging over the $\boldsymbol{n}(\boldsymbol{x})$ orientations.

There have been many measurements of the nematic order parameter in aligned nematic elastomers, in which case a variety of experimental techniques are available. The alignment in these materials can be installed in two ways: (1) by applying a uniaxial field (usually mechanical stress) to an original polydomain texture and passing through the polydomain-monodomain transition [12, 17], or (2) by crosslinking the network in a state uniformly aligned by a mechanical, electric, or surface field [18, 19]. In both cases, of course, one does not expect a true phase transition and indeed all the reports find the varying degrees of supercritical crossover, see [20, 21] and references therein.

In contrast, we deliberately devise the physical system as close as possible to the equilibrium 'nematic glass' state. Apart from crosslinking the network in a fully isotropic state, carefully avoiding any stray aligning influences, we also choose the type of crosslinking that is creating as weak as possible orientational effect (cf. Fig. 6). There have been many reports showing that using a more robust rod-like crosslinking group results in much stronger orientational effect and possibly undermines the approximations required for the continuum coarse-graining of the random-anisotropy field. It would be very interesting to conduct comparative studies, with varying the characteristics of random field by changing crosslinking density and molecular structure. However, in this first study we concentrate on the system where we are safely within the limits of weak random field, and the resulting 'nematic glass' phase. There are two key results we report here. First of all, after careful analysis of the D-NMR signal, we are able to obtain the temperature dependence of the equilibrium local order parameter $S(T)$, which has

a clear critical behavior $S \propto |T - T_c|^{0.22}$ according to our best fit. This was the principal aim of our study. However, in addition, we found that the NMR line width (which reflects the loss of local spin mobility) has a very clear λ-shaped peak at the transition point T_c. We associate this peak with the critical growth of correlation length of fluctuations on both sides of the transition, which further supports the conclusion about the continuum transition from the isotropic into the 'nematic glass' phase.

Deuterium NMR analysis

The spin Hamiltonian for deuterium in a high magnetic field $\boldsymbol{B}_0$ is dominated by the Zeeman and quadrupolar interactions [22] with the latter amenable to a first order perturbation theory calculation in order studies. In the absence of motion a carbon bound deuterium gives rise to a doublet absorption spectra centered at the Larmor precession frequency and with a splitting given by

$$w = \frac{6\pi}{2}\nu_Q \left(\frac{3}{2}\cos^2\theta - \frac{1}{2} + \frac{1}{2}\eta\sin^2\theta\cos 2\phi\right) \tag{1}$$

where θ and ϕ are the polar and azimuthal angles that define the orientation of the external magnetic field in the principal frame of the electric field gradient (EFG) tensor V_{ij} at the nucleus site. The characteristic frequency scale $\nu_Q = (eQ/h)V_{zz}$ is called the quadrupolar coupling constant which for sp^2 bonds is $\approx$185 kHz [25] (e is the electron charge, Q – quadrupolar moment of ^{2}H nucleus, and h the Planck constant). $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the biaxial asymmetry parameter, which is small and negligible here. In a polydomain sample the contributions from all θ, ϕ orientations generate a characteristic spectral pattern that for a 3D powder average is known as a 'Pake pattern' [26] which allows a direct measurement of the time-averaged $\overline{\nu}_Q$. The corresponding EFG tensor component is directly related to the orientational nematic order parameter via $\overline{V}_{zz} = v^m S$, where v^m is a constant for a given molecule [27]. The Pake spectra

were fitted to the doublet expression:

$$G(\omega) = \int_{\Omega} \left[h(\omega - \tfrac{1}{2}w(\theta, \phi, \overline{\nu}_Q), \Delta\omega, \alpha) + h(\omega + \tfrac{1}{2}w(\theta, \phi, \overline{\nu}_Q), \Delta\omega, \alpha) \right] \sin\theta d\theta d\phi \quad (2)$$

using a conjugate directions method [23], where $w(\theta, \phi, \overline{\nu}_Q)$ is given by (1) in the dynamic case, the splitting amplitude $\overline{\nu}_Q$ and the individual line width $\Delta\omega$ are fitting parameters, and $h(\omega, \Delta\omega, \alpha)$ is the specific line shape function.

The doublet and powder spectra discussed above are formed by single and multiple pairs of structured lines, respectively, determined by the transverse relaxation occurring in the system [24]. When the correlation time τ_c of the fluctuating quadrupolar interaction is small, $\tau_c\nu_Q \ll 1/(2\pi)$ (the fast-motion limit), the line structure acquires a Lorentzian form corresponding to an exponentially decaying transverse magnetization in the rotating frame, e^{-t/T_2^*}. Here T_2^* is the decay time of transverse magnetization related to the frequency width at half height $\Delta\omega$ of the Lorentzian line by $T_2^* = 2/\Delta\omega$:

$$h(\omega) = \text{FT}\left\{e^{-t/T_2^*}\right\} \equiv \frac{T_2^*}{1 + (T_2^*\omega)^2}. \quad (3)$$

As the molecular motion slows down, the coherence between the nuclear spins reduces faster, making the spins precess at different frequencies (larger $\Delta\omega$); in real time the correlation between the signals from the different spins reduces and the NMR signal decays faster (smaller T_2^*). In the opposite, slow-motion limit, $\tau_c\nu_Q \gg 1/(2\pi)$, a Gaussian shape becomes a good approximation for the line structure [22], given by the Fourier transform of

$$h(\omega) = \text{FT}\left\{e^{-(t/\tau_g)^2}\right\} \equiv \sqrt{\pi}\,\tau_g\,e^{-\omega^2\tau_g^2/4} \quad (4)$$

where the signal decay time τ_g is related to the frequency width by $\tau_g = 4\sqrt{\ln 2}/\Delta\omega$. Figure 1 gives the composite representation of a sequence of D-NMR scans on cooling from the isotropic state, illustrating the widening of the central peak, and then the emergence of characteristic nematic splitting. It is very important to note the complete absence of any coexistence, which
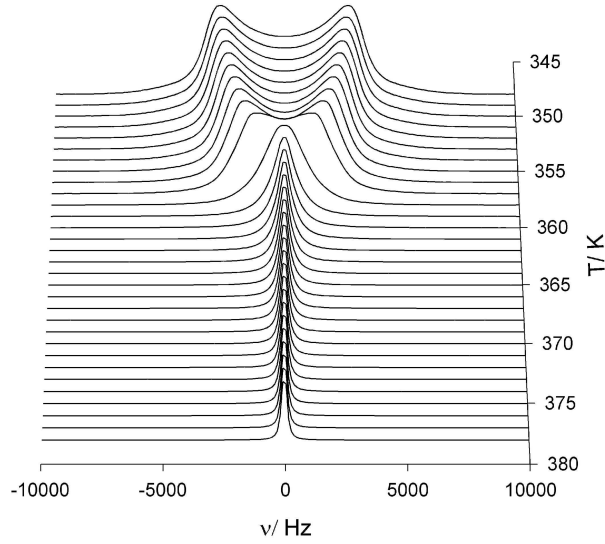
Figure 1: **D-NMR spectra on changing temperature**. Composite representation of Pake spectra evolution on cooling the system from the isotropic state. Note the absence of any coexistence between the emerging nematic splitting and the isotropic central peak.

is a necessary feature of a first-order transition and which has been observed in previous NMR experiments on nematic elastomers [20, 21] (which, for various reasons, always had a local stress frozen into the network preventing critical fluctuations).

It was suggested by Brereton and others [28, 29, 30, 31] that in isotropic polymer networks, even in the absence of an ordering field, the averaging of second-rank tensorial interactions from nuclear spins is not complete due to the local anisotropy imposed by crosslink constraints. Nematic interactions between chain segments have also been shown to contribute to the widening of spectra. This gives rise to the prediction of a characteristic absorption spectra with a cusp at zero frequency [28, 30, 31]. In our case, the deuterium labels are placed in the mesogenic units, away from the backbone and these constraints are expected to have a small effect on the NMR line shape, contributing at most to increase the line width in a weakly temperature dependent mode. Indeed the high-temperature spectra closely follow the classical Lorentzian shape.

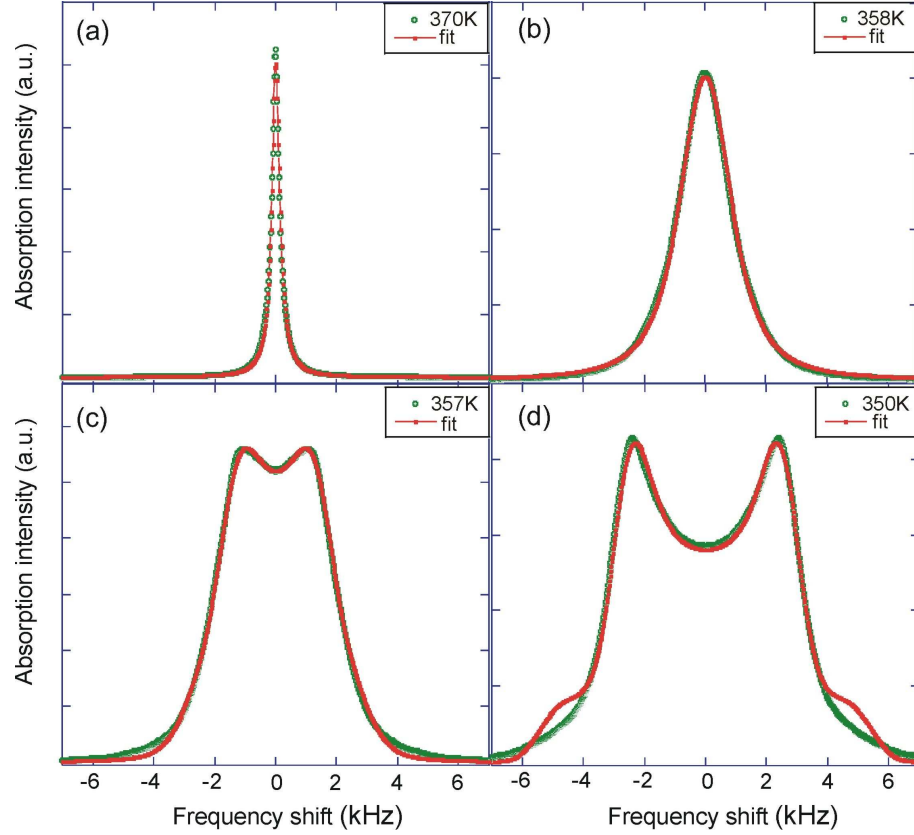Figure 2 gives the more detailed absorption spectra obtained in the D-NMR experiment

Figure 2: **Fitting D-NMR spectra**. Plots show the raw data for D-NMR spectra at several key temperatures (labelled on plots), above and below the phase transition point. The fits are obtained by the combined Lorentzian-Gaussian model discussed in the text. Later in the paper we shall find the nematic transition point $T_c = 358.01$K, so it is important to see no splitting in (b) and a pronounced splitting in (c), with no co-existence effects as in [20, 21].
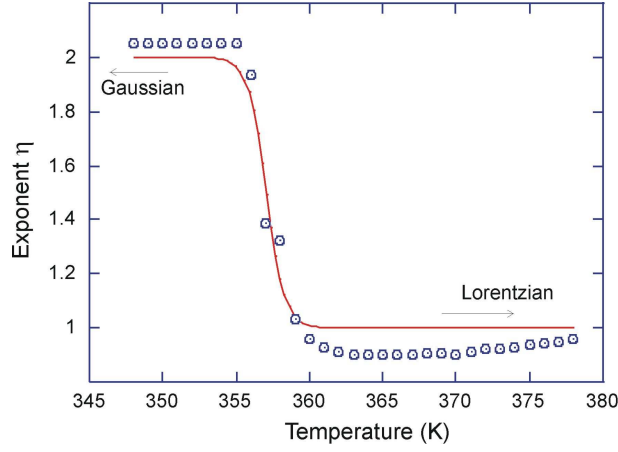
Figure 3: **Lorentzian vs. Gaussian NMR line**. The values of exponent α obtained from a three-parameter fit ($\circ$) are plotted for each temperature. Clearly the values of $\alpha = 1$ and 2 are approached far from the transition point. The solid line is the best fit by (5), which we then use as the fixed value for $\alpha(T)$ function.

in characteristic regimes. The high-temperature isotropic phase has a narrow line that closely matches the Lorentzian form, Fig. 2(a), as expected in a classical process of fast rotational diffusion. In the nematic phase molecular motion slows down and collective modes set in and the orientational relaxation time of mesogenic groups attached to the polymer backbone increases significantly. In a low molecular weight nematic this time is typically of the order of several times 10^{-7}s, which is very much shorter than the characteristic time of NMR. Measurements of rotational viscosity γ_1 [32, 33], which is proportional to the relaxation time [34, 35], show an increase of over 4 orders of magnitude in the nematic phase of elastomers, comparing to the low-molecular weight nematics. This suggests that the correlation time of rod-like groups attached to the backbone becomes closer to the characteristic NMR time $(2\pi\nu_Q)^{-1}$, as soon as the nematic mean field sets in; indeed we find that the Gaussian form is more appropriate to describe the line structure in the nematic phase.

In order to test fitting the NMR spectra in the whole temperature range we have applied a model with the variable exponent $\alpha(T)$, numerically Fourier-transforming $\exp\left[-\pi\left(t\,\Delta f\right)^\alpha\right]$.

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Figure 3 shows the results for the fitted empirical exponent $\alpha(T)$. It is clear that the basic expectation of the crossover between the Lorentzian regime in the isotropic phase ($\alpha \approx 1$ at $T > T_c$) crosses over to the Gaussian regime in the nematic phase at $T < T_c$, where $\alpha \approx 2$. To reduce the unnecessary freedom of multi-parameter fitting, we choose to assign a fixed form to the variable exponent $\alpha(T)$ so that it describes the fundamental crossover between $\alpha = 1$ and 2, as shown in the plot:

$$\alpha(T) = 1.5 - 0.5 \tanh \left[\frac{T - T^*}{m} \right] . \tag{5}$$

The closest fit is achieved with $T^* = 357.1$K and the width of temperature crossover $m = 1.62$K. Note that (as we shall see below) the actual critical point of the transition is about a degree higher, $T_c = 358$K. This shift is natural, since the crossover from the diffusive to the slow-relaxation regime (Lorentzian to Gaussian line shape) occurs when the local nematic mean field grows sufficiently strong to slow down the molecular rotation rate closing in the characteristic NMR frequency. With this choice of $\alpha(T)$ we only have two fitting parameters, $\overline{\nu}_Q$ and $\Delta\omega$, which are obtained as functions of temperature. The quality of line fits is very good in the relevant sections, as is evident from Fig. 2, although the long tails of the peaks at very low temperatures deviate slightly as illustrated in the (d) plot for 350K.

Nematic-isotropic transition

Having established the rules of analysis of our D-NMR signal, we then proceed with fitting the Pake pattern (2) to all the spectra. In this fitting we only allow two free parameters: the average quadrupolar coupling constant, $\overline{\nu}_Q$, and the characteristic width of the distribution, $\Delta\omega \equiv 2\pi\Delta f$. The first parameter gives directly the magnitude of the nematic order $S(T)$, in this case defined as the time-average of orientational motion of individual rod-like units. In the non-ergodic system such as polydomain "nematic glass" it is essential to distinguish between this, and the spatially averaged quantities (such the outputs of X-ray, or optical dischroism mea-
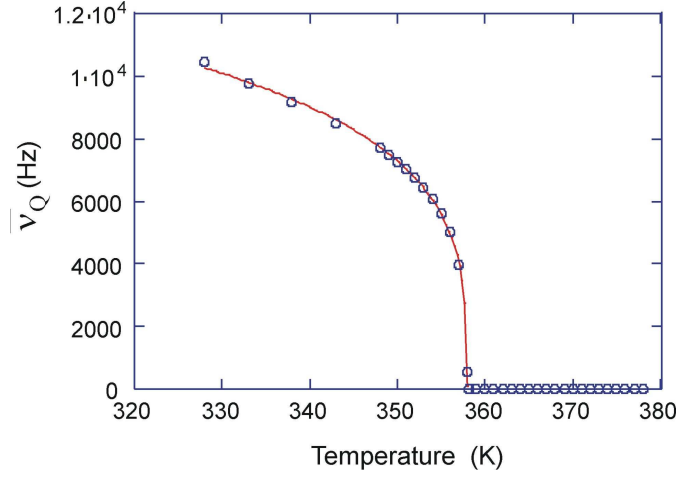
Figure 4: **Nematic order parameter**. Plot of the average quadrupolar coupling constant $\overline{\nu}_Q$, obtained from a 2-parameter fit of each spectrum, against temperature. Apart from a constant dimensional factor, $\overline{\nu}_Q$ directly represents the local nematic order parameter $S(T)$.

surements). There is an effective averaging of the output signal over the sample volume, but in the NMR experiment it takes place after the field of the tensor order parameter $Q_{ij}(\boldsymbol{r})$ is established at every point at each temperature. In this sense, our analysis is based on the assumption [13] that the scalar value of S is uniform throughout the polydomain director texture in the sample. If this was not the case, i.e. the magnitude of the nematic order varied in space (e.g. across domain boundaries or in disclination cores), then our clean double-peak Pake pattern would not be observed deep in the nematic phase. This alone is a very important observation, making a stark contrast with the classical Schlieren texture of a disclination-coarsening nematic liquid [36].

Figure 4 shows the fitted values of $\overline{\nu}_Q$ against temperature. It is clear, as it was visually apparent from the shape of NMR peaks in figure 1, that the nematic order sets in in a critical fashion. The fit to the data suggests the variation $S \propto |T - T_c|^{0.22}$, with the critical point $T_c = 358.01$K. Importantly, the fitting gives values $S = 0$ above T_c unambiguously, indicating that no supercritical or "paranematic" effects take place in our system. This is another important
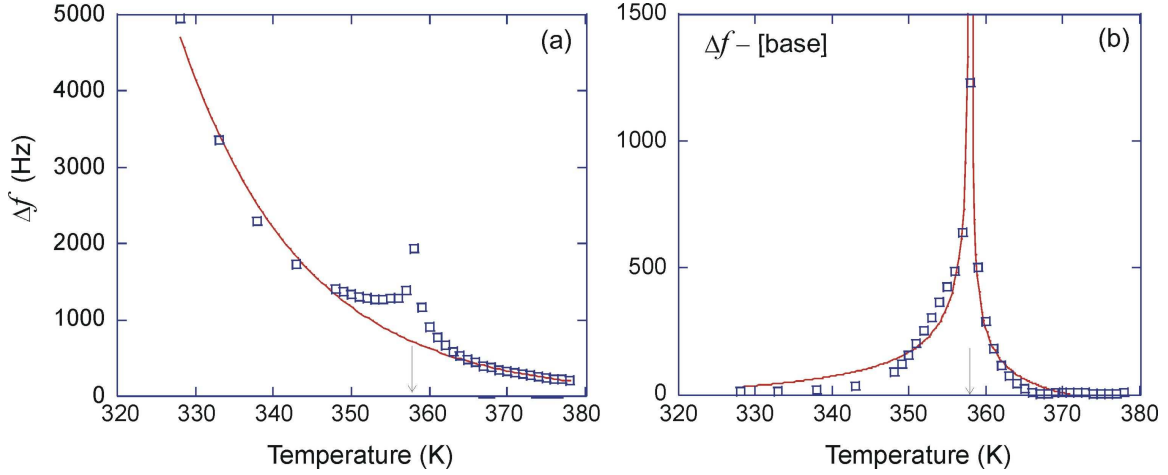
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Figure 5: **Critical fluctuations**. (a) Plot of the frequency width $\Delta f \equiv \Delta\omega/2\pi$, obtained from a 2-parameter fit of each spectrum, against temperature. The solid line is a baseline fit for a polymer network that gradually approaches its glass transition, resulting in reduced segment mobility and the associated widening of the spectra. (b) Plot of the frequency width with the baseline subtracted, illustrating the particular widening during the transition. The solid line on both sides of T_c is a fit by $|T - T_c|^{-0.5}$, as in Landau-Ginzburg model of critical divergence of fluctuation correlation length.

point, contrasting with many other studies. It is well-known that monodomain (macroscopically aligned, crosslinked under uniaxial external field) nematic elastomers have a diffuse supercritical transition, with its sharpness decreasing with more rigid crosslinkers or higher external fields imposed at formation. The recent detailed calorimetric study [21] gives the details of this, and the earlier literature. There are very few studies of polydomain systems, and none that examine the soft un-entangled networks (obtain by de-swelling, with small flexible crosslinks). Due to our preparation, the system we study here is close to true criticality, which is a remarkable effect of quenched random-anisotropy disorder considering that the underlying quadrupolar nematic ordering is a first-order transition.

The second evidence for the critical transition is found in the behavior of our second fitting parameter: the distribution width $\Delta\omega$, which is proportional to the correlation time of

orientational motion of mesogenic groups. Figure 5(a) shows the increase of $\Delta\omega$ on cooling the elastomer network. There are clearly two separate effects: the overall increase representing the slowing down of molecular motion on approaching the structural glass transition in a polymer network, and the pronounced peak around the phase transition. The solid line in figure 5(a) shows the exponential fit of the baseline data to the Vogel-Fulcher exponential $\Delta\omega \propto \exp[A/(T - T_\beta)]$, with $A = 3200$ and $T_\beta = 120$K. It is not unexpected to find the cutoff temperature T_β so much lower than the "ordinary" polymer glass transition $T_g \approx 300$K in our material: the latter represents the so-called α-relaxation, or freezing of the polymer backbone motion. Our NMR experiment probes the motion of side-groups, that is β- or even γ-relaxation, which freezes at much lower temperatures. Importantly, this baseline increase is continuous across both the Lorentzian and the Gaussian regimes on both sides of the nematic transition.

Figure 5(b) plots the $\Delta\omega$ peak around the transition, with the baseline polymer dynamics taken out. The solid lines on both sides of T_c are fits to the critical $|T - T_c|^{-b}$, using the value $T_c = 358.01$K from the analysis in figure 4 and returning the same exponent $b = 0.5$ on both sides of T_c. We suggest that this behavior represents the growth of correlations of critical fluctuations near the transition point. As the size of correlated nematic fluctuations increases near the critical point, $\xi \propto |T - T_c|^{-\nu}$, the time for (collective) re-orientation of rod-like units within this volume increases proportionally. Curiously, the exponent we obtain from the best fit is very close to the mean-field $\nu = 1/2$, which connects with the earlier discussion of the mean-field approximation and the de Almeida-Thouless line.

Summary

A detailed study of deuterium NMR in polydomain nematic elastomers suggests that the structure of this state is analogous to random-anisotropy spin glass. Because of this analogy, the results for the local symmetry breaking, order parameter and fluctuations near the phase transition

have a broad significance for the whole field. The local magnitude nematic order parameter is homogenous throughout the system in spite of the director correlations being short-range in the replica-symmetric approximation. Analysis of NMR lines at different temperatures suggests that the transition from the isotropic high-temperature phase is of continuous critical nature. Since this transition (quadrupolar order with weak quenched random-anisotropy field) has not been studied with renormalization group, we cannot assign any particular significance to the apparent critical exponents for the order parameter magnitude, $S \propto |T - T_c|^{0.22}$ and correlation length of critical fluctuations, $\xi \propto |T - T_c|^{-0.5}$. However, the fact that we see an apparent critical behavior in a system that undergoes a first-order transition in its pure state is of remarkable importance. This could be the first experimental study that confirms the Aizenman-Wehr theorem predicting such an effect. Secondary findings of this work, on the continuous change between the Lorentzian and Gaussian NMR line shape and on the continuous slowing down of β-relaxation of polymer side-groups on cooling the elastomer, are also of great interest in their respective fields.

Methods

Preparation. All starting materials and samples of side chain siloxane liquid crystalline elastomers were prepared in the Cavendish Laboratory following the hydrosilation procedures developed by H. Finkelmann [37]. The polymer backbone was a poly-methylhydrosiloxane with approximately 60 Si-H units per chain, obtained from ACROS Chemicals. The pendant mesogenic groups were 4'-methoxyphenyl-4-(1-buteneoxy) benzoate (MBB), as illustrated in figure 6, attached to the backbone via the reaction of of Si-H group with the vinyl bond. For good quality deuterium NMR signal, we used 50% of the MBB units with the fully deuterated outer benzene ring. All networks were chemically crosslinked via the same reaction, in the presence of commercial platinum catalyst COD, obtained from Wacker Chemie, with the flexible
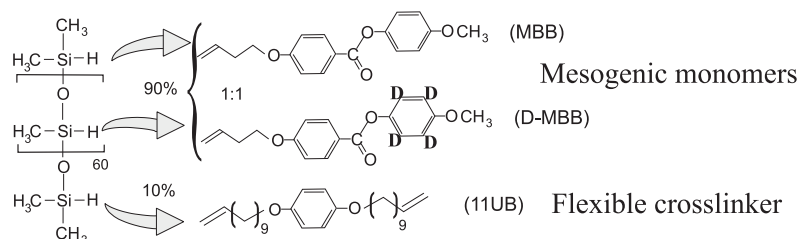
Figure 6: **Composition of nematic elastomer**. The classical polysiloxane nematic elastomer is obtain by attaching the rod-like mesogenic units (MBB) to the flexible siloxane chain. 50% of these units were deuterated (D-MBB), symmetrically to preserve the molecular symmetry as shown in the sketch. Permanent network crosslinking has been achieved by reacting with 2-functional flexible molecule 11UB, which attaches to two backbone chains.

di-functional crosslinking group 1,4 di(11-undeceneoxy)benzene (11UB) also shown in Fig. 6. The crosslinking density was calculated to be 10 mol% of the reacting bonds in the siloxane backbone, so that on average each chain has 9 mesogenic groups between crosslinking sites.

Our aim has been to obtain a true polydomain state of the nematic phase, which can only be generated when the crosslinking is fully random and no internal stresses of entanglements are frozen into the resulting network. For this, we have completed the crosslinking reaction in the highly swollen (in toluene) isotropic phase of the polymer. After the completion of all reactions, the samples were slowly de-swollen so that the dry elastomer network did not end up over-entangled.

Testing procedure.

The NMR data was collected using a Bruker Avance II+ 300 MHz spectrometer working at a resonance frequency for deuterium of 46.1 MHz. The solid echo sequence with a pulse separation of 20μs and a $\pi/2$ pulse width of 5μs was used to obtain the NMR spectra in a high power, wide line, probe head. The elastomer sample consisting of a thin stripe of material was placed over holding glass rods evenly placed horizontally within a cylindrical teflon case. The measurements where performed after having heated the sample up to 378K (more than 15K

above the nematic-isotropic transition) at a rate of 5K/min. After a stabilization period of 30 min the first measurement of the highest-temperature state was taken. Upon conclusion, the sample was slowly cooled, at a rate of 1K/min, to the second temperature to be analyzed, followed by an equilibration time delay of 10 min at this temperature. Consecutive NMR measurements were obtained on decreasing the temperature from 378K to 348K, at 1K intervals, all preceded by the identical equilibration procedure. At lower temperatures, down to 328K, further measurements were recorded 5K apart. Four thousand scans (with a recycle delay of 500ms) were collected in each measurement to reach acceptable signal to noise ratios.

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